



# Few-layered MoS<sub>2</sub> vertically aligned on 3D interconnected porous carbon nanosheets for hydrogen evolution

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## ABSTRACT

MoS<sub>2</sub> has been considered as a non-precious alternative to platinum based electrocatalyst for electrochemical hydrogen evolution. Since most of the active site exists on the edges of MoS<sub>2</sub>, a material design that could increase the exposure of the edges could improve its catalytic activity. In this work, we prepared small sized and few-layered MoS<sub>2</sub> that is vertically aligned on three-dimensional interconnected porous carbon nanosheets (IPC). Benefiting from exposure of MoS<sub>2</sub> edges, MoS<sub>2</sub>/IPC composite exhibits a high catalytic activity (225 mA cm<sup>-2</sup> at -250 mV vs. RHE, and Tafel slope of 38 mV dec<sup>-1</sup>) and maintains steady performance for several hours. Since the procedure to prepare MoS<sub>2</sub>/IPC composites is scalable and cost-effective, our method of preparing few-layered MoS<sub>2</sub> on porous carbon shows great potential as a competitive electrocatalysts for HER.

## 1. Introduction

Hydrogen has been considered to be a clean energy carrier towards the future. Unfortunately, hydrogen is mainly produced via reforming fossil fuels resulting in major byproducts such as greenhouse gases [1–3]. Electrochemical water splitting powered by a renewable energy is an eco-friendly way to produce hydrogen without emission of greenhouse gas; however the costs in relation to production cost imposes severe limitation to practical applicability. For hydrogen evolution reaction (HER), which occurs at the cathode part of the electrochemical water splitting cell, rare and expensive Platinum (Pt) based noble-metal electrocatalysts exhibits the best performance up to date. To be practical for industrial use, developing a low cost and high performing cost efficient electrocatalyst with high performance that can replace Pt-based material in production is essential [4–11].

Among the economical materials that have been investigated as Pt replacements for HER catalysis, MoS<sub>2</sub> shows promising results in regards to low cost [12], electrochemical stability [13], and high theoretical catalytic activity [14–20]. As of now, there are two major hindering factors in relation to catalytic performance of MoS<sub>2</sub>: First, MoS<sub>2</sub> has a small number of active sites since the thermodynamically favored basal plane is catalytically inert [21,22]. In addition, terminal sulfide

groups at the edges of the MoS<sub>2</sub> layers has been regarded as catalytically active sites for HER. Second, MoS<sub>2</sub> has low electrical conductivity to supply the electrons to the active sites. [23–25] Therefore, synthesizing nanostructured MoS<sub>2</sub> nanosheets on conductive substrate could be an effective strategy to overcome the aforementioned obstacles.

Recently, significant efforts were made to prepare small sized MoS<sub>2</sub> with fewer layers [26–31]. Through this approach, the terminating sulfide groups at the edges of the MoS<sub>2</sub> can have maximum exposure and electrons can be easily transferred to the active edges by shortening the electron transport path. An alternative to improve the catalytic performance of MoS<sub>2</sub> is by preparing vertically aligned MoS<sub>2</sub> nanosheets on conductive support, which can increase the exposure of active edges [32–36]. Several groups demonstrated that the catalytic performance of vertically aligned MoS<sub>2</sub> nanosheets is much higher compared to randomly aligned MoS<sub>2</sub> nanosheets [32,33]. In addition, expanding interlayers of MoS<sub>2</sub> is an alternative strategy that can further enhance the catalytic activity of MoS<sub>2</sub>. According to the theoretical studies, increasing the interlayer spacing of MoS<sub>2</sub> nanolayers can decrease hydrogen adsorption energy at the edges, which is favorable for catalyzing HER. Therefore, although preparing small sized and few-layered interlayer expanded MoS<sub>2</sub> nanosheets vertically aligned on conductive supports are quite challenging, it is the ideal way to enhance

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catalytic activity of MoS<sub>2</sub>.

Porous carbons had received remarkable attention due to their excellent electrochemical properties, low cost, and stability. Especially, high surface area of porous carbon has been used as a conductive support to immobilize nanosized material [37–39]. For MoS<sub>2</sub>, it is reported that the interaction between MoS<sub>2</sub> precursors and pores on carbon surface enables growth of highly dispersed MoS<sub>2</sub> nanoparticles [40,41]. As a reference, Liao et al. [41] used mesoporous graphene as both catalyst support and template to prepare MoS<sub>2</sub> nanodots. However, in these reports, the prepared few-layered MoS<sub>2</sub> nanosheets were horizontally positioned on porous carbon. As the active sites of MoS<sub>2</sub> nanosheets exist at the edges of the basal plane, horizontally supported MoS<sub>2</sub> nanosheet is not an effective design for exposing active edges.

In this paper, we prepared few-layered and vertically aligned MoS<sub>2</sub> by employing 3D interconnected porous carbon (IPC) with rich micro-, meso-, and macropores as conductive support. The micropores on the carbon surface play a role providing anchoring sites to deposit the few-layered MoS<sub>2</sub> nanosheets. As the composite material is composed of small-sized and few-layered MoS<sub>2</sub> nanosheets, MoS<sub>2</sub>/IPC-2 exhibits high catalytic activity, which was comparable to most of MoS<sub>2</sub>/carbon electrocatalysts. The synthesis described in this paper is scalable and cost-effective; therefore, our method of preparing few-layered and vertically aligned MoS<sub>2</sub> is expected to be extended to a wide range of applications [42–44], including HER catalysts.

## 2. Experimental section

### 2.1. Synthesis of IPC

IPC was prepared through pyrolyzing potassium citrate under inert gas according to the method reported by Sevilla et al. [45]. Typical synthesis begins with grinding 3 g of potassium citrate with mortar to produce a fine powder. The precursor was thermally decomposed under Ar atmosphere up to 850 °C at a heating rate of 3 °C/min and held at that temperature for 2 h. After thermal treatment, the product was treated with hydrochloric acid to dissolve the remaining unreacted precursors. Next, the resultants were collected by centrifugation, followed by washing with water and ethanol three times. Finally, the products were lyophilized for several days to obtain fine powder. The obtained product was denoted as IPC.

### 2.2. Solvothermal synthesis of MoS<sub>2</sub>/IPC composite

In a typical synthesis, 10 mg of IPC, and 20 mg of (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> were dispersed in 10 mL of *N,N*-dimethylformamide (DMF) with the aid of ultrasonication for 30 min. After making a clear solution, it was transferred to 20 mL Teflon line autoclave and heated in an electrical oven at 200 °C for 10 h. The product (MoS<sub>2</sub>/IPC-2) was washed several times with DI water and ethanol and dried overnight in 60 °C oven. In comparison, the weight ratio of IPC to (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> varied from 1:1 and 1:4 while keeping the amount of IPC the same and denoted as MoS<sub>2</sub>/IPC-1 and MoS<sub>2</sub>/IPC-4, respectively. Bare MoS<sub>2</sub> was synthesized under a similar condition to MoS<sub>2</sub>/IPC-2 without adding IPC.

### 2.3. Physical characterization

The morphology of the samples was analyzed using Hittachi S-4800 field emission scanning electron microscopy (FE-SEM). Samples were prepared by drop-casting a diluted suspension of a material in ethanol on an aluminum foil and electrically connected (Carbon tape) to an SEM stub. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images were recorded using JEOL JEM-2010 operating at 300 kV. Samples were drop-casted from diluted ethanol dispersions of a material on a holey carbon coated 300 mesh Cu grids and dried using IR lamp. X-ray diffraction (XRD) patterns were tested by Bruker D8 advance superspeed powder

diffractometer with Cu K $\alpha$  radiation operating at 40 kV and 25 mA at a scan rate of 3° min<sup>-1</sup>. Raman spectra were recorded by Renishaw Invia Raman spectroscopy equipped with a 514 nm excitation laser. The elemental composition of the catalysts was analyzed by using a wavelength dispersive X-ray Fluorescence (XRF) spectrometer II (Bruker, S8 TIGER).

X-ray photoelectron spectroscopy (XPS) were measured by Thermo Escalab 250 Xi system (Thermo Scientific) with a monochromated Al K $\alpha$  as the emission source at power of 150 W (14.9 kV  $\times$  8.79 mA). The total pressure in the main vacuum chamber during analysis was approximately  $9 \times 10^{-9}$  mbar. Samples were filled into shallow wells of a custom-made sample holder and analyzed at an emission angle of 0° as measured from the surface normal. As the actual emission angle is ill-defined in the case of powders (ranging from 0–90°), the sampling depth may range from 0 to 10 nm. Binding energies were calibrated to the adventitious carbon C 1s peak at 284.8 eV. XPS curve was fitted using Thermo Advantage software V5.978. The areas of the Mo 3d<sub>3/2</sub> and 3d<sub>5/2</sub> peaks were constrained to maintain a ratio of 2:3 during the fitting of the Mo 3d XPS spectra. For S 2p XPS spectra, the areas were constrained to ensure a proper 1:2 area ratio between the S 2p<sub>1/2</sub> and 2p<sub>3/2</sub> peaks.

Small angle X-ray scatter (SAXS) measurements have been performed on powder samples using a Nanostar U small-angle X-ray scattering system (Bruker, Germany) using Cu K $\alpha$  radiation (40 kV, 35 mA) with wavelength of 0.154 nm. Scattering of the samples was acquired in the range of  $0.05 < q < 7 \text{ nm}^{-1}$ . The formula  $d = 2\pi/q$  was used to calculate the *d*-spacing values. Brunauer–Emmett–Teller (BET) analysis was carried out at –196 °C using ASAP 2020. Before the measurements, samples were dried at 100 °C for 4 h.

### 2.4. Electrochemical measurement

All electrochemical measurements were performed with a standard three-electrode setup that consists of Ag/AgCl filled with saturated KCl as a reference electrode, graphite rod as a counter electrode, and glassy carbon rotating disk electrode (RDE) modified with active materials as a working electrode. Before modifying the electrode, the glassy carbon surface was polished with 1.0 and 0.3  $\mu\text{m}$  Al<sub>2</sub>O<sub>3</sub> powders with a wet polishing pad. After polishing, remaining Al<sub>2</sub>O<sub>3</sub> powders on the glassy carbon surface was thoroughly washed with water and sonicated in water for about 1 min. Additionally, RDE was rotated at 2400 rpm. Nitrogen saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> (pH 0.3) was used as an electrolyte.

5 mg of catalyst for testing was dispersed in a mixture of 440  $\mu\text{L}$  of DI water, 440  $\mu\text{L}$  of DMF, and 120  $\mu\text{L}$  of Nafion (5 wt%, Aldrich) and ultrasonicated for 30 min to make a homogeneous slurry. Then, 10  $\mu\text{L}$  of the catalyst containing slurry was drop-casted on glassy carbon electrode (GCE, diameter of 5 mm) with a loading mass of 0.254 mg cm<sup>-2</sup> and dried using an infrared lamp.

All electrochemical measurements without Electrochemical Impedance Spectroscopy (EIS) analysis were held in Metrohm Autolab workstation PGSTAT 302 N. To add, the data was corrected to compensate iR losses during the measurements. The electrochemical catalytic activity of the catalysts was measured by using linear sweep voltammetry (LSV) with scan rate of 2 mV s<sup>-1</sup>. To condition the electrodes, 30 cyclic voltammetry scans were conducted between 0 and -0.3 V (V vs. RHE) prior to LSV measurements. Double layer capacitance (related to the electrochemical surface of the catalyst) was measured at a potential range of 0.2 V to 0.3 V (V vs. RHE) by varying scan rate from 20 mV s<sup>-1</sup> to 70 mV s<sup>-1</sup> using CV. EIS was measured with electrochemical analyzer ZIVE SP1 with frequency ranging from 0.1 Hz to 10<sup>6</sup> Hz with an amplitude of 5 mV. To measure stability of the electrode, CV measurement was held in potential range of -0.3 to 0.2 V (V vs. RHE) with a scan rate of 50 mV s<sup>-1</sup>. All measurement are measured respect to reversible hydrogen electrode according to following equation:  $E (\text{V vs. RHE}) = E (\text{V vs. Ag/AgCl}) + 0.197 + 0.0591 \times \text{pH}$ .

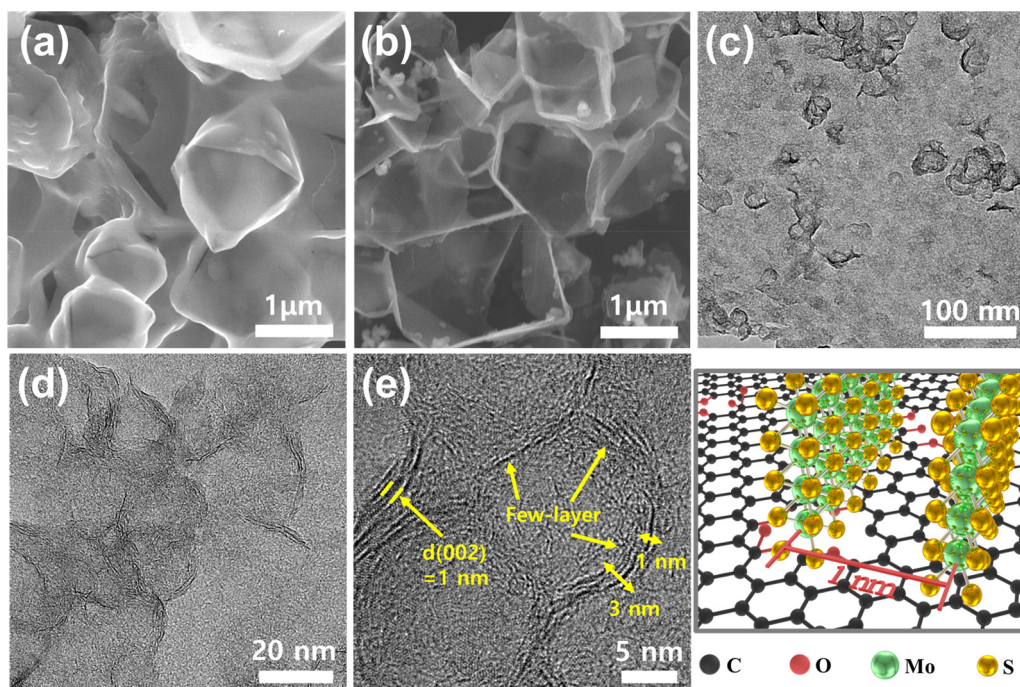


Fig. 1. SEM images of (a) IPC and (b) MoS<sub>2</sub>/IPC-2; (c) Low- and (d, e) high-magnification TEM images and (f) XRD patterns of sample MoS<sub>2</sub>/IPC-2.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of catalysts

The MoS<sub>2</sub>/IPC composite was prepared via a two-step synthetic. The synthesis begins with preparation of IPC. IPC was prepared according to the method developed by Sevilla et al. [45] with slight modifications. Then, MoS<sub>2</sub> nanosheets were deposited on the IPC through solvothermal reducing (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> in DMF. (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> has been used as a source for both Mo and S. Since DMF has reducing ability under solvothermal condition, MoS<sub>4</sub><sup>2−</sup> ions are reduced into MoS<sub>2</sub> [46].

Fig. 1 shows the morphologies of IPC and MoS<sub>2</sub>/IPC composite formed from a 1:2 wt ratio of molybdenum sulfide precursor to IPC (MoS<sub>2</sub>/IPC-2). As shown in Fig. 1a, IPC consists of several irregularly 3D interconnected nanosheets, with dimensions of several micrometers. Fig. 1b–e shows the SEM and TEM images of the MoS<sub>2</sub>/IPC-2. It is observable that the morphology of the IPC is retained with nanometer sized few-layered MoS<sub>2</sub> grown on its surface. Morphology of MoS<sub>2</sub> synthesized without IPC support was flower-shaped, which confirms the role of IPC acting as a support material to form vertically aligned MoS<sub>2</sub> (Fig. S1). The HR-TEM image in Fig. 1e shows that MoS<sub>2</sub> layers are fewer than 3 layers while having interlayer distance (along the (002) direction) of ~1 nm, which is larger than the interlayer spacing of typical 2H-MoS<sub>2</sub> (0.615 nm). Meanwhile, large number of defects were observed in few-layered MoS<sub>2</sub> nanosheets.

The enlarged interlayer spacing of MoS<sub>2</sub>/IPC-2 was also observed in X-ray diffraction (XRD) measurements. For MoS<sub>2</sub>/IPC-2, diffraction peaks near 9.4° and 18.7°, which correspond to (002) and (004), are found (Fig. 2a). The highly symmetric diffraction peak at 9.4° reveals that MoS<sub>2</sub> layers are highly ordered along the c-axis. In reference to Bragg's law, the interlayer spacing along the (002) direction is determined to be approximately 1 nm, which is consistent with the value determined from the HR-TEM results. Since the solvothermal reaction is performed at a relatively short duration and low temperature of 200 °C, formation of defects in MoS<sub>2</sub> lattices are expected and is thought to be the cause of the interlayer expansion [47]. The number of layers was estimated by the Scherrer's equation from the (002) diffraction peak [48]. For bare MoS<sub>2</sub> and MoS<sub>2</sub>/IPC-2 composite, the average number of

layers were estimated to be approximately, 4.61 nm and 3.23 nm, which is consistent to the TEM results (Fig. S1, Fig. 1e).

The chemical structure of the MoS<sub>2</sub>/IPC composite is characterized by XPS (Fig. S3a). In Mo 3d spectrum of the MoS<sub>2</sub>/IPC-2 (Fig. 3c), two characteristic peaks are located at 232.21 and 229.16 eV, which arises from Mo<sup>4+</sup> 3d<sub>3/2</sub> and Mo<sup>4+</sup> 3d<sub>5/2</sub>, respectively, are found. This result indicates that Mo<sup>4+</sup> was dominant in MoS<sub>2</sub>/IPC-2. In addition to Mo<sup>4+</sup> state, peaks (236.01 eV, 232.96 eV, 233.31 eV, 229.96 eV) with high valence Mo states (Mo<sup>6+</sup>, Mo<sup>5+</sup>) are found (Fig. 3a, e). Since significant amount of high valence Mo states (Mo<sup>6+</sup>, Mo<sup>5+</sup>) are found, we think that molybdenum oxide in form of MoO<sub>3-x</sub> or in molybdenum oxysulfide coexists with MoS<sub>2</sub> nanosheets according to result of previous studies. This form of molybdenum oxide is commonly observed when MoS<sub>2</sub> is slightly oxidized [49]. Fig. 3d shows the S 2p spectra of the MoS<sub>2</sub>/IPC-2. In S 2p spectra, the peaks at 163.17 and 164.32 eV can be indexed to bridging S<sub>2</sub><sup>2−</sup> and apical S<sup>2−</sup> of MoS<sub>2</sub> whereas the peaks at 162.01 and 163.11 eV can be attributed to terminal S<sub>2</sub><sup>2−</sup> of MoS<sub>2</sub> (Fig. 3b, f). In C 1s spectra of MoS<sub>2</sub>/IPC-2 (Fig. S3b), peak located at 286.7 eV, assigned to C–O bonding, was also found [50]. The O 1s spectra can be de-convoluted to three peaks at 530.9, 531.9 and 533 eV (Fig. S3c). The existence of MoO<sub>3-x</sub> or molybdenum oxysulfide species was also verified in Raman spectra of MoS<sub>2</sub>/IPC-2. In Fig. 2b, the Raman spectra of both MoS<sub>2</sub>/IPC-2 and bare MoS<sub>2</sub> exhibit B<sub>2g</sub> and B<sub>1g</sub> vibration modes of Mo–O bonds. In addition to vibration modes of Mo–O bonds, characteristic modes (in-plane Mo–S phonon mode (E<sub>2g</sub>), out-of-plane Mo–S mode (A<sub>1g</sub>)) of MoS<sub>2</sub> were found which verifies existence of molybdenum sulfide species [51,52].

IPC with large amount of micropores and large specific surface area (SSA) were utilized as supporting material. Since few-layered MoS<sub>2</sub> are grown on the surface of IPC, decrease in SSA was expected. In this study, the pore structures of samples were measured by a Braunauer-Emmett-Teller (BET) nitrogen adsorption/desorption method. As in Fig. 4a, the nitrogen sorption isotherms of IPC can be categorized as of typical type I, meaning that the pores were mainly composed of micropores. Compared to IPC, MoS<sub>2</sub>/IPC-2 displayed widen knee of the isotherm, which indicates that the micropore quantity decreased as the MoS<sub>2</sub> is deposited on the carbon surface [45]. The SSA and pore volume of IPC was 1723 m<sup>2</sup> g<sup>−1</sup> and 0.91 cm<sup>3</sup> g<sup>−1</sup>, respectively. After

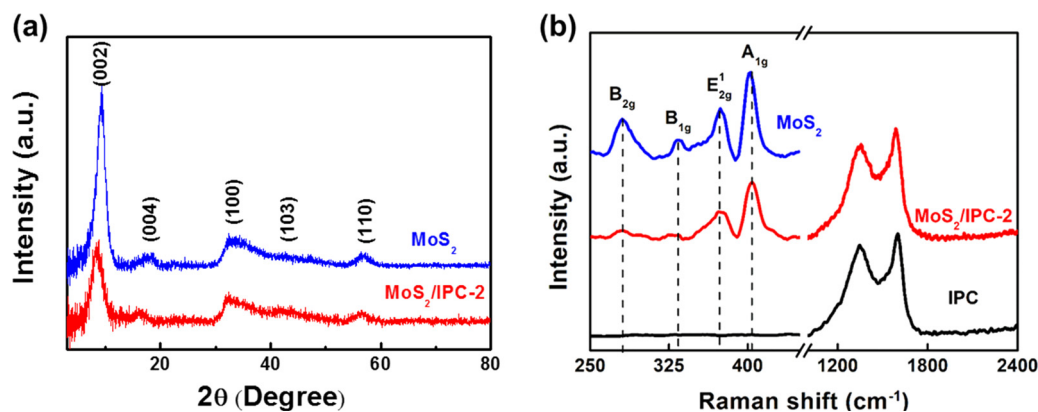


Fig. 2. (a) XRD patterns of bare MoS<sub>2</sub> and MoS<sub>2</sub>/IPC-2 and (b) Raman spectra of bare MoS<sub>2</sub>, MoS<sub>2</sub>/IPC-2 and IPC.

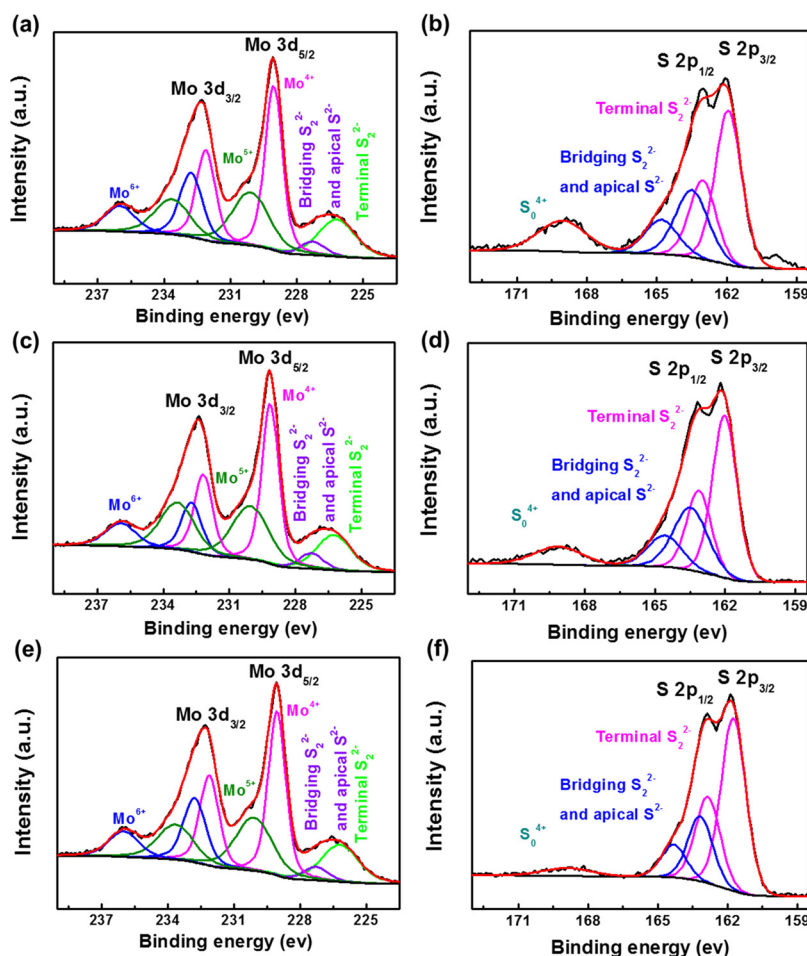


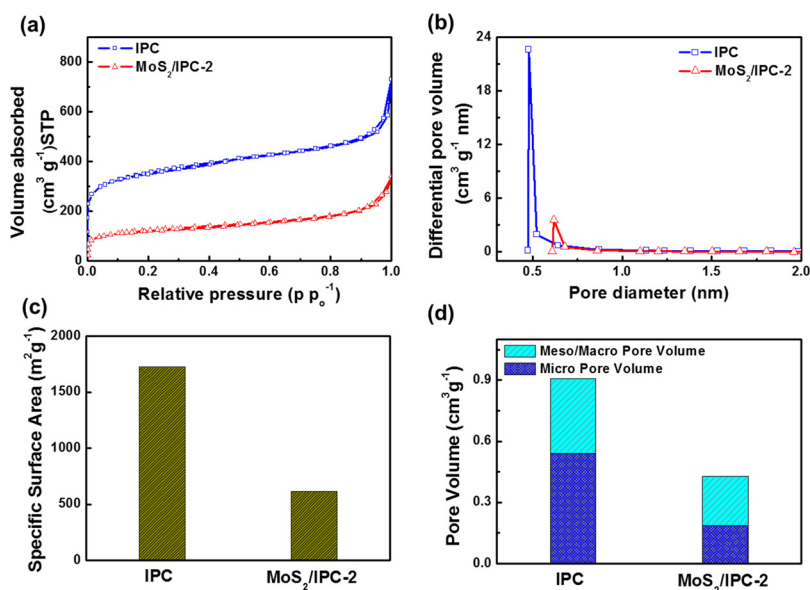
Fig. 3. High-resolution Mo 3d and S 2p spectrum for (a, b) MoS<sub>2</sub>/IPC-1, (c, d) MoS<sub>2</sub>/IPC-2, and (e, f) MoS<sub>2</sub>/IPC-4.

deposition of MoS<sub>2</sub> on IPC surface, the SSA and pore volume became 616 m<sup>2</sup> g<sup>−1</sup> and 0.43 cm<sup>3</sup> g<sup>−1</sup>, respectively. This was confirmed by analyzing pore size distribution (Fig. 4b) determined by the density function theory (DFT) method. Pore size distribution graph clearly reveals that the micropore volume ( $V_{\text{micro}}$ ) is decreased and volume portion of meso/macropore ( $V_{\text{meso/macro}}$ ) increased after deposition of MoS<sub>2</sub> on IPC. To note, significant decrease in  $V_{\text{micro}}$  to  $V_{\text{meso/macro}}$  ratio of IPC was observed, which implies that large portion of micropore is occupied by the growth of MoS<sub>2</sub> on its surface. The BET SSA and pore volume of composites are summarized in Fig. 4c, d and Table S2.

Pore structure of bare MoS<sub>2</sub>, IPC and MoS<sub>2</sub>/IPC-2 were also characterized by SAXS (Fig. S5a). It has been reported that peaks from

$q = 3.14 \text{ nm}^{-1}$  ( $d$ -spacing of 2 nm) to  $q = 6.4 \text{ nm}^{-1}$  ( $d$ -spacing of 0.98 nm) is the micropore range [53]. In this range, IPC has the highest scattering intensity followed by MoS<sub>2</sub>/IPC-2 and bare MoS<sub>2</sub>. Decreased scattering intensity after deposition of MoS<sub>2</sub> on IPC indicates that large portion of micropores is decreased which is consistent to the nitrogen adsorption observations. Unlike IPC and MoS<sub>2</sub>/IPC-2, bare MoS<sub>2</sub> displayed lowest scattering intensity in the micropore range. This result indicates that bare MoS<sub>2</sub> does not have any micropores.

From the nitrogen adsorption analysis and SAXS, significant decrease in both specific surface area and micropore volume was observed. Since the morphology of IPC did not change after growth of MoS<sub>2</sub> nanosheets on its surface, significant decrease in micropore

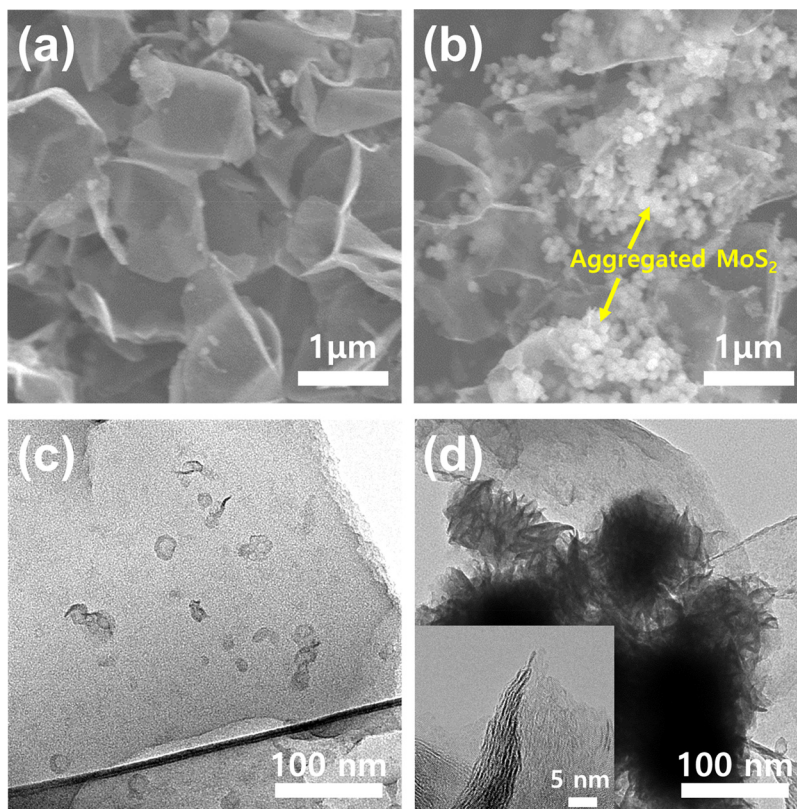


**Fig. 4.** (a) Nitrogen adsorption-desorption isotherms for IPC and  $\text{MoS}_2/\text{IPC-2}$ ; (b) Pore size distribution curves for IPC and  $\text{MoS}_2/\text{IPC-2}$ ; (c) Specific surface area and (d) pore volume for IPC and  $\text{MoS}_2/\text{IPC-2}$ .

volume can be understood as an evidence that deposited  $\text{MoS}_2$  occupied the micropores and micropores served as nucleation sites for  $\text{MoS}_2$  nanosheets. Research conducted by Liao et al. [54] and Liu et al. [40] also had shown that the edges of micropores on carbon surface can be used as a template to prepare nanostructured  $\text{MoS}_2$ .

IPC with different loading amount of  $\text{MoS}_2$  nanosheets was prepared with same procedure by tuning the weight ratio of IPC/ $\text{MoS}_2$  precursor from 1:1, 1:2, to 1:4. We designate the various  $\text{MoS}_2/\text{IPC}$  composite as “ $\text{MoS}_2/\text{IPC-x}$ ”, whereas x refers to weight ratio of IPC to  $\text{MoS}_2$

precursor. Fig. 5 shows the corresponding morphology of the prepared  $\text{MoS}_2/\text{IPC}$  composites. As shown in Fig. 5a, b, presence of IPC can be seen in both  $\text{MoS}_2/\text{IPC-1}$  and  $\text{MoS}_2/\text{IPC-4}$ . In contrast,  $\text{MoS}_2/\text{IPC-4}$ , aggregated  $\text{MoS}_2$  nanosheets forming nanoflower is observed. TEM image of  $\text{MoS}_2/\text{IPC-4}$  (Fig. 5d) reveals that these nanoflowers are comprised of ~5 layers of  $\text{MoS}_2$  nanosheets. Unlike  $\text{MoS}_2/\text{IPC-4}$ , few-layered  $\text{MoS}_2$  grown on carbon surface is observed in  $\text{MoS}_2/\text{IPC-1}$  (Fig. 5c). However, compared to TEM image of  $\text{MoS}_2/\text{IPC-4}$  above, much lower density of the few-layered  $\text{MoS}_2$  nanosheets is observed in



**Fig. 5.** SEM and TEM images of (a, c)  $\text{MoS}_2/\text{IPC-1}$  and (b, d)  $\text{MoS}_2/\text{IPC-4}$ .

MoS<sub>2</sub>/IPC-1.

X-ray fluorescence spectroscopy (XRF) was used to determine the mass loading and composition of MoS<sub>2</sub> deposited on the carbon support (Table S1). According to XRF analysis, weight percentage of MoS<sub>2</sub> in the composites increases as the amount of MoS<sub>2</sub> precursor increases. Meanwhile, atomic ratio of determined by the XRF analysis shows that loaded MoS<sub>2</sub> on all MoS<sub>2</sub>/IPC composites was sulfur deficient which supports the existence of MoO<sub>3-x</sub> or molybdenum oxysulfide [49,55]. Interestingly, as the amount of MoS<sub>2</sub> precursor increased, MoS<sub>2</sub> in the MoS<sub>2</sub>/IPC composites became less sulfur deficient. Unlike MoS<sub>2</sub>/IPC composites, bare MoS<sub>2</sub> showed S/Mo atomic ratio of 2.09. In previous reports, small sized MoS<sub>2</sub> nanosheets have been reported to be more susceptible to oxidation than bulk MoS<sub>2</sub> [56–59]. Decreased S/Mo atomic ratio upon decreasing amount of MoS<sub>2</sub> precursor further supports that MoS<sub>2</sub> formed on MoS<sub>2</sub>/IPC composites exhibits much smaller dimension than bare MoS<sub>2</sub>.

The detailed oxidation state of Mo species in bare MoS<sub>2</sub> and MoS<sub>2</sub>/IPC composites was further studied by comparing relative percentages of Mo<sup>4+</sup>: Mo<sup>5+</sup>: Mo<sup>6+</sup> in Mo 3d region of XPS [60]. For MoS<sub>2</sub>/IPC-1, relative ratios from the XPS intensities was 26.98:53.54:19.48 at. %, confirming that significant proportion of Mo species is oxidized (Table S2). Moreover, oxidized sulfur species was verified in S2p spectra of MoS<sub>2</sub>/IPC composites (Fig. 3b, d, f). Unlike MoS<sub>2</sub>/IPC-1, relative percentages of Mo<sup>4+</sup>: Mo<sup>5+</sup>: Mo<sup>6+</sup> of bare MoS<sub>2</sub> was 44.49:51.29:4.22. Upon increasing MoS<sub>2</sub> loading from MoS<sub>2</sub>/IPC-2 to MoS<sub>2</sub>/IPC-4, it is clearly observed that the portion of Mo<sup>6+</sup> in Mo 3d spectra is significantly decreased which can be attributed to increased size of MoS<sub>2</sub>, which is consistent to SEM results above. Meanwhile, it is interesting to note that large fraction of Mo species in MoS<sub>2</sub>/IPC-2 is composed of Mo<sup>5+</sup> species. Since the conductivity of molybdenum sulfide is related to oxidation state of Mo, large fraction of Mo<sup>5+</sup> species implies that MoS<sub>2</sub> in MoS<sub>2</sub>/IPC-2 composite is expected to exhibit high electron conductivity. Compared to MoO<sub>3</sub>, oxygen deficient MoO<sub>3-x</sub> has been reported to show several orders of magnitudes increase in conductivity [61,62].

In previous reports [63], it was found that the ratio between terminal S<sub>2</sub><sup>2-</sup> and bridging S<sub>2</sub><sup>2-</sup>/apical S<sup>2-</sup> is highly dependent on the size of MoS<sub>2</sub> nanosheets. A higher ratio of terminal S<sub>2</sub><sup>2-</sup> to bridging S<sub>2</sub><sup>2-</sup>/apical S<sup>2-</sup> indicates smaller size of MoS<sub>2</sub>. For MoS<sub>2</sub>/IPC composites, the ratio of terminal S<sub>2</sub><sup>2-</sup> to bridging S<sub>2</sub><sup>2-</sup>/apical S<sup>2-</sup> decreased accordingly as the amount of the MoS<sub>2</sub> precursor increased (Fig. 3b, d, f), (MoS<sub>2</sub>/IPC-1: 3.04, MoS<sub>2</sub>/IPC-2: 2.37, MoS<sub>2</sub>/IPC-4: 2.08). However, as observed from TEM images above, the density of the few layered MoS<sub>2</sub> decreased by decreasing the amount of precursor.

### 3.2. Electrocatalytic properties of MoS<sub>2</sub>/IPC composite

Catalytic activity of the synthesized MoS<sub>2</sub>/IPC composites measured in an N<sub>2</sub>-purged 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte using standard three-electrode measurements by depositing the electrocatalyst on a glassy carbon electrode (GCE). The optimum catalyst loading on the glassy carbon electrode was 0.254 mg cm<sup>-2</sup> (Fig. S6). We used Pt wire (0.5 mm diameter) as a reference because it exhibits the highest catalytic activity of any known material.

The polarization curves of MoS<sub>2</sub>/IPC-1, MoS<sub>2</sub>/IPC-2, MoS<sub>2</sub>/IPC-4, IPC and bare MoS<sub>2</sub> normalized by area of the electrode shown on Fig. 6a. As expected, Pt wire showed excellent HER activity with a nearly zero overpotential whereas IPC showed negligible HER activity. Every MoS<sub>2</sub> containing samples exhibited high catalytic activity; MoS<sub>2</sub>/IPC-2 shows the best catalytic activity with a high current density of 225 mA cm<sup>-2</sup> at an overpotential of 250 mV. In contrast, MoS<sub>2</sub> containing samples synthesized under different conditions (i.e. MoS<sub>2</sub>/IPC-1, MoS<sub>2</sub>/IPC-4, and bare MoS<sub>2</sub>) showed lower current densities (i.e. 84 mA cm<sup>-2</sup>, 83 mA cm<sup>-2</sup>, and 15 mA cm<sup>-2</sup>, respectively) at overpotentials of 250 mV (Fig. 6a, c, Table S5). Large differences in catalytic activity between bare MoS<sub>2</sub> and MoS<sub>2</sub>/IPC composites indicate

that IPC could increase electron transportation to active sites existing at the edges of nanosheets. The differences in catalytic activities among the MoS<sub>2</sub>/IPC composites may be ascribed to differences in number of exposed active edges formed according to different weight ratios of MoS<sub>2</sub> precursor IPC. To compare the intrinsic catalytic activity of MoS<sub>2</sub>/IPC composites, the MoS<sub>2</sub> mass activity of the above catalysts were calculated. Fig. S11 compares the mass-normalized HER performances of MoS<sub>2</sub>/IPC composites. At overpotential of 200 mV, MoS<sub>2</sub>/IPC-2 exhibits highest catalytic current of 400 mA mg<sup>-1</sup> followed by 185 mA mg<sup>-1</sup> of MoS<sub>2</sub>/IPC-1 and 115 mA mg<sup>-1</sup> of MoS<sub>2</sub>/IPC-4, demonstrating that the intrinsic catalytic activity of MoS<sub>2</sub>/IPC-2 is much higher than that of MoS<sub>2</sub>/IPC-4 and MoS<sub>2</sub>/IPC-1. The catalytic activity of MoS<sub>2</sub>/IPC-2 normalize by the MoS<sub>2</sub> mass surpasses most of the MoS<sub>2</sub>/carbon electrocatalysts enlisted in Table S5 which indicates that few-layered MoS<sub>2</sub> deposited on IPC exhibits high intrinsic catalytic activity despite its oxidized state.

To further study the detailed HER kinetics of MoS<sub>2</sub>/IPC composites and bare MoS<sub>2</sub>, Tafel plots were constructed by converting the polarization curves to graphs of the logarithm of the cathodic current versus the overpotential (Fig. 6b). The Tafel plots were analyzed by fitting the Tafel equation to the linear regions. The Tafel equation is:

$$\eta = b \log(j) + a \quad (1)$$

where  $a$  is the exchange current and  $b$  is the Tafel slope. The Tafel slope is a parameter that can diagnose HER mechanisms occurring at the surface of the electrocatalyst. For MoS<sub>2</sub>, wide range of Tafel slopes has been reported. The primary reason for this is that Tafel slope is largely dependent on electrical conductivity, crystallinity of the MoS<sub>2</sub> and surface area of the catalyst. The obtained Tafel slopes for bare MoS<sub>2</sub>, MoS<sub>2</sub>/IPC-1, MoS<sub>2</sub>/IPC-2, and MoS<sub>2</sub>/IPC-4 were 64, 40, 38, and 43 mV dec<sup>-1</sup> respectively (Fig. 6c). All MoS<sub>2</sub>/IPC composites exhibited similar low Tafel slopes near 40 mV dec<sup>-1</sup>, which suggests that the Volmer-Heyrovsky reaction mechanism is occurring on the MoS<sub>2</sub>/IPC composites [17]. Work done by Li et al. [64] demonstrated that the terminal disulfide groups at the edges of the low crystalline MoS<sub>2</sub> are responsible for low Tafel slope. The slight differences in Tafel slope among the MoS<sub>2</sub>/IPC composites may ascribed to differences in electrical conductivity and surface area of the catalyst [65,66].

The electrochemical surface area (ECSA) was estimated by measuring the double layered capacitance ( $C_{dl}$ ) in non-Faradaic potential region (Fig. 6d, Fig. S7). Since very significant area of carbon support is not covered by MoS<sub>2</sub>, the capacitance values cannot be directly correlated to the number of active sites [67]. However, measured capacitance values may be used to roughly estimate the total surface of the catalyst modified electrode. MoS<sub>2</sub>/IPC-1 had the highest capacitance value of 16.67 mF cm<sup>-2</sup> followed by MoS<sub>2</sub>/IPC-2 at 16.22 mF cm<sup>-2</sup>, MoS<sub>2</sub>/IPC-4 at 11.48 mF cm<sup>-2</sup>, and bare MoS<sub>2</sub> at 4.60 mF cm<sup>-2</sup>. MoS<sub>2</sub>/IPC-4 showed lowest capacitance value due to presence of large numbers of aggregated multilayered MoS<sub>2</sub> on its surface. Despite the highest capacitance value, MoS<sub>2</sub>/IPC-1 exhibited lowest catalytic current density. This may be resulted by decreased mass transportation for high surface area catalyst lacking electrocatalytically active sites [65].

The electrochemical impedance spectroscopy (EIS) measurements were conducted to characterize the interface reactions and kinetics of HER. Fig. 7a shows Nyquist plots of bare MoS<sub>2</sub> and MoS<sub>2</sub>/IPC composites. The Nyquist plot was fitted to a corresponding equivalent circuit of two CPE (constant phase element) model, which consist of electrolyte resistance in series with two parallel R-CPE elements (Fig. S10). For two CPE model, high-frequency semicircle is related to the surface porosity whereas the low frequency is related to the charge transfer process. Two CPE model is composed of following circuit elements:  $R_s$  is attributed to the solution resistance, CPE is related to the double-layer capacity of the electrodes,  $R_c$  and charge transfer resistance ( $R_{ct}$ ) are related to the porous structure and the reaction kinetics of the HER, respectively. MoS<sub>2</sub>/IPC-2 had the smallest  $R_{ct}$  of 10.14  $\Omega$  compared to 16.75  $\Omega$  for MoS<sub>2</sub>/IPC-1, 14.70  $\Omega$  for MoS<sub>2</sub>/IPC-4 and 43.74  $\Omega$  for bare

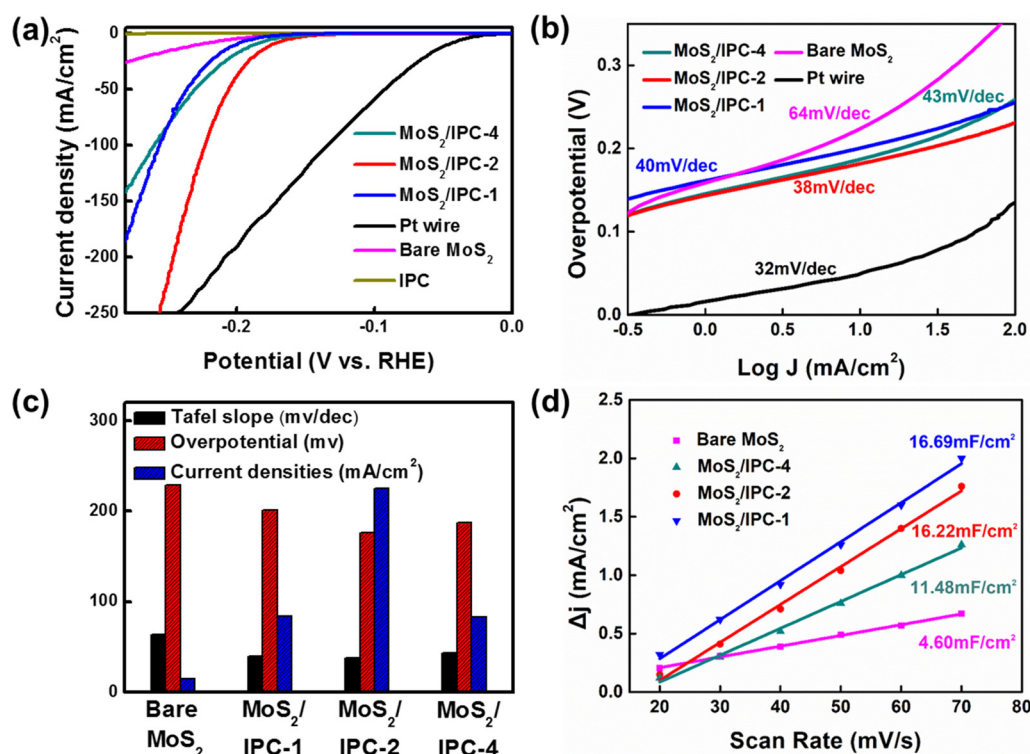


Fig. 6. (a) HER polarization curves and (b) Tafel plot of corresponding catalyst of bare MoS<sub>2</sub>, MoS<sub>2</sub>/IPC composites, IPC and Pt wire; (c) Comparison of Tafel slope (black), overpotential (red) at 10 mAcm<sup>-2</sup>, and current density (blue) at overpotential 250 mV of bare MoS<sub>2</sub> and MoS<sub>2</sub>/IPC composites; (d) Summary of ECSA by measuring cyclic voltammetry measurements for bare MoS<sub>2</sub> and MoS<sub>2</sub>/IPC composites (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

MoS<sub>2</sub> (Fig. 7a, Table S4). MoS<sub>2</sub>/IPC composites exhibit lower  $R_{ct}$  than bare MoS<sub>2</sub>, which can be attributed to IPC acting as conductive support in the composites. From the following result, we verified that MoS<sub>2</sub>/IPC-2 is the optimum electrocatalyst having the least  $R_{ct}$  from catalyst to reactants. It is important to note that MoS<sub>2</sub>/IPC-4 exhibits lower  $R_{ct}$  than MoS<sub>2</sub>/IPC-1. This difference in  $R_{ct}$  between MoS<sub>2</sub>/IPC-1 and

MoS<sub>2</sub>/IPC-4 may arise from low density of few-layered MoS<sub>2</sub> and high surface area of MoS<sub>2</sub>/IPC-1 forming thick film on current collector as we explained from ECSA results.

To assess the long term stability of MoS<sub>2</sub>/IPC-2, cyclic voltammetry scans (1000 cycles) and constant current input ( $-10 \text{ mA cm}^{-2}$ ,  $-50 \text{ mA cm}^{-2}$ ) was held. MoS<sub>2</sub>/IPC-2 exhibits negligible catalytic loss

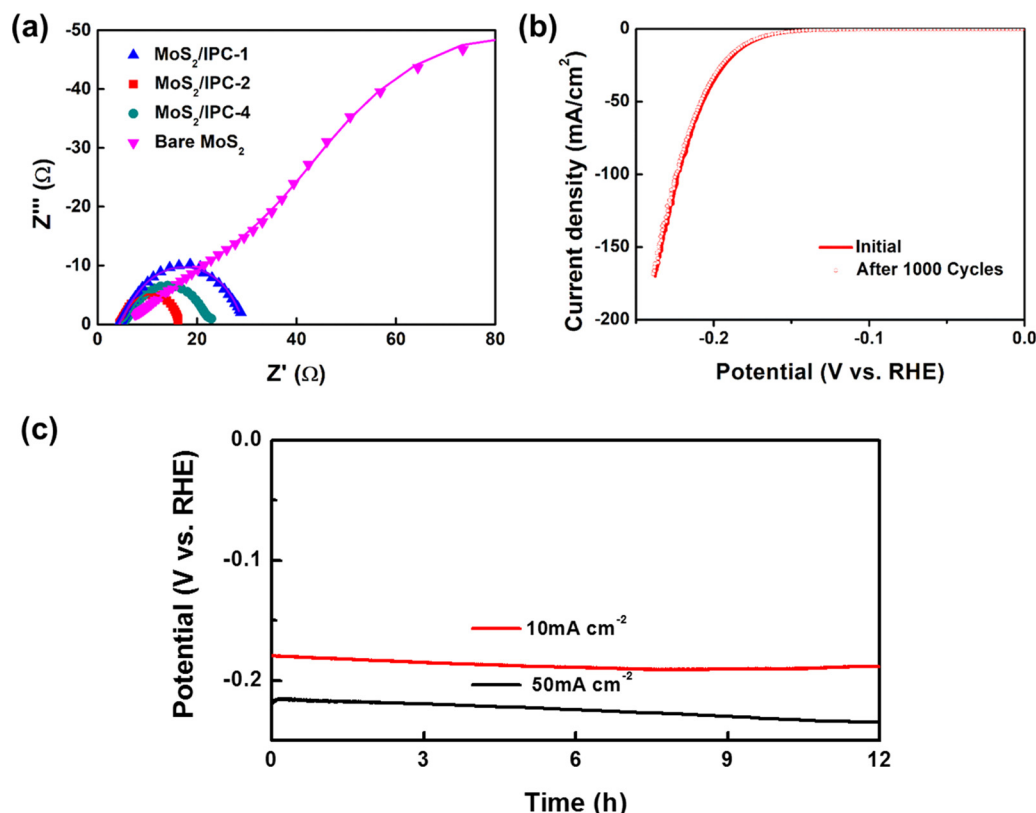


Fig. 7. (a) Nyquist plots of bare MoS<sub>2</sub> and MoS<sub>2</sub>/IPC composites; (Symbols are experimental data and continuous lines are data fitted by the 2CPE model) (b) Polarization curves of MoS<sub>2</sub>/IPC-2 before and after 1000th cycle; (c) Galvanostatic cycle stability test on MoS<sub>2</sub>/IPC-2 under current density of  $-10 \text{ mA cm}^{-2}$  and  $-50 \text{ mA cm}^{-2}$ .

even after 1000 cyclic voltammetry (CV) cycles between -0.3 V and 0.2 V vs. RHE at a scan rate of 50 mV s<sup>-1</sup> (Fig. 7b). The long-term stability of MoS<sub>2</sub>/IPC-2 was assessed through the chronopotentiometry test under constant current input of -10 mA cm<sup>-2</sup> and -50 mA cm<sup>-2</sup> (Fig. 7c). At -50 mA cm<sup>-2</sup>, MoS<sub>2</sub>/IPC-2 exhibited a constant curve with a ~ 20 mV increase in the overpotential after 12 h whereas chronopotentiometry test held at -10 mA cm<sup>-2</sup> shows negligible increase in overpotential. This implies that the MoS<sub>2</sub>/IPC-2 exhibits good electrochemical stability during HER.

In comparison with the catalytic activity of MoS<sub>2</sub>/IPC composites by means of different indicators, we found that MoS<sub>2</sub>/IPC-2 had the most optimal catalytic performance. Although MoS<sub>2</sub>/IPC-1 had the smallest MoS<sub>2</sub> which was supported by highest ratio of terminal S<sub>2</sub><sup>2-</sup> to bridging S<sub>2</sub><sup>2-</sup>/apical S<sup>2-</sup> and TEM results, low density of few-layered MoS<sub>2</sub> may result in lowest catalytic activity among the MoS<sub>2</sub>/IPC composites. Moreover, significant portion of Mo species in MoS<sub>2</sub>/IPC-1 was oxidized which has been reported to be detrimental for HER performance [68]. For MoS<sub>2</sub>/IPC-4, despite the large portion of unoxidized Mo species, amount of aggregated MoS<sub>2</sub> increased which causes difficulties to expose its catalytically active edges.

The excellent electrochemical HER catalytic performance of optimized MoS<sub>2</sub>/IPC composite (MoS<sub>2</sub>/IPC-2) can be attributed to three factors: (1) High density of few-layered MoS<sub>2</sub> nanosheets expose a significant amount of catalytically active edges. (2) The optimized morphology of MoS<sub>2</sub>/IPC-2 composite facilitates mass transport and electrical conductance. (3) Reduced sizes of MoS<sub>2</sub> nanosheets decreases charge transfer resistance which leads an increased in catalytic activity. Conclusively, MoS<sub>2</sub>/IPC-2 as a low-cost and high-performance catalyst shows promise for use in HER electrocatalysts in practical applications.

#### 4. Conclusion

In summary, a composite material consisting of few-layered MoS<sub>2</sub> supported on 3D interconnected porous carbon was developed as an efficient HER electrocatalyst. The formation of few-layered MoS<sub>2</sub> may be ascribed to micropores on IPC surface acting as nucleation sites. Overall, due to the high density few-layered MoS<sub>2</sub> with less aggregation, the optimized catalyst MoS<sub>2</sub>/IPC-2 exhibited high HER activity with a large cathodic current density (225 mAcm<sup>-2</sup> at 250 mV), small Tafel slope of 38 mV dec<sup>-1</sup> and long-term durability. The synthesis in this work presents an overall cost-effective approach to produce high density few-layered MoS<sub>2</sub> on a conductive support; consequently, this synthetic approach can also be extended to other applications that require few-layered MoS<sub>2</sub>.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.02.035>.

#### References

- [1] M.S. Dresselhaus, I.L. Thomas, Alternative energy technologies, *Nature* 414 (2001) 332–337.
- [2] J.A. Turner, Sustainable hydrogen production, *Science* 305 (2004) 972.
- [3] P. Lianos, Review of recent trends in photoelectrocatalytic conversion of solar energy to electricity and hydrogen, *Appl. Catal. B-Environ.* 210 (2017) 235–254.
- [4] D.S. Kong, J.J. Cha, H.T. Wang, H.R. Lee, Y. Cui, First-row transition metal dichalcogenide catalysts for hydrogen evolution reaction, *Synth. Lect. Energy Environ. Technol. Sci. Soc.* 6 (2013) 3553–3558.
- [5] Y. Zheng, Y. Jiao, Y.H. Zhu, L.H. Li, Y. Han, Y. Chen, A.J. Du, M. Jaroniec, S.Z. Qiao, Hydrogen evolution by a metal-free electrocatalyst, *Nat. Commun.* 5 (2014).
- [6] Z.W. Chen, D. Higgins, A.P. Yu, L. Zhang, J.J. Zhang, A review on non-precious metal electrocatalysts for PEM fuel cells, *Synth. Lect. Energy Environ. Technol. Sci. Soc.* 4 (2011) 3167–3192.
- [7] J. Deng, P.J. Ren, D.H. Deng, L. Yu, F. Yang, X.H. Bao, Highly active and durable non-precious-metal catalysts encapsulated in carbon nanotubes for hydrogen evolution reaction, *Synth. Lect. Energy Environ. Technol. Sci. Soc.* 7 (2014) 1919–1923.
- [8] Y.J. Ko, J.M. Cho, I. Kim, D.S. Jeong, K.S. Lee, J.K. Park, Y.J. Baik, H.J. Choi, W.S. Lee, Tungsten carbide nanowalls as electrocatalyst for hydrogen evolution reaction: New approach to durability issue, *Appl. Catal. B-Environ.* 203 (2017) 684–691.
- [9] S.-K. Park, J.K. Kim, Y. Chan Kang, Metal-organic framework-derived CoSe<sub>2</sub>/(NiCo)Se<sub>2</sub> box-in-box hollow nanocubes with enhanced electrochemical properties for sodium-ion storage and hydrogen evolution, *J. Mater. Chem. A Mater. Energy Sustain.* 5 (2017) 18823–18830.
- [10] J.K. Kim, G.D. Park, J.H. Kim, S.K. Park, Y.C. Kang, Rational design and synthesis of extremely efficient macroporous CoSe<sub>2</sub>-CNT composite microspheres for hydrogen evolution reaction, *Small* 13 (2017).
- [11] Z. Mo, H. Xu, Z. Chen, X. She, Y. Song, J. Lian, X. Zhu, P. Yan, Y. Lei, S. Yuan, H. Li, Construction of MnO<sub>2</sub>/Monolayer g-C<sub>3</sub>N<sub>4</sub> with Mn vacancies for Z-scheme overall water splitting, *Appl. Catal. B* 241 (2019) 452–460.
- [12] A.B. Laursen, S. Kegnaes, S. Dahl, I. Chorkendorff, Molybdenum sulfides-efficient and viable materials for electro- and photoelectrocatalytic hydrogen evolution, *Synth. Lect. Energy Environ. Technol. Sci. Soc.* 5 (2012) 5577–5591.
- [13] M. Ledendecker, J.S. Mondschein, O. Kasian, S. Geiger, D. Gohl, M. Schalenbach, A. Zeradjanin, S. Cherevko, R.E. Schaak, K. Mayrhofer, Stability and activity of non-noble-metal-based catalysts toward the hydrogen evolution reaction, *Angew. Chem. Int. Ed.* 56 (2017) 9767–9771.
- [14] B. Hinnemann, P.G. Moses, J. Bonde, K.P. Jorgensen, J.H. Nielsen, S. Horch, I. Chorkendorff, J.K. Nørskov, Biomimetic hydrogen evolution: MoS<sub>2</sub> nanoparticles as catalyst for hydrogen evolution, *J. Am. Chem. Soc.* 127 (2005) 5308–5309.
- [15] J. Liu, Y. Liu, D. Xu, Y. Zhu, W. Peng, Y. Li, F. Zhang, X. Fan, Hierarchical “nanoroll” like MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> hybrid with high electrocatalytic hydrogen evolution activity, *Appl. Catal. B Environ.* 55 (2019) 2078–2081.
- [16] Y.Z. Liu, H.Y. Zhang, J. Ke, J.Q. Zhang, W.J. Tian, X.Y. Xu, X.G. Duan, H.Q. Sun, M.O. Tade, S.B. Wang, 0D (MoS<sub>2</sub>)/2D (g-C<sub>3</sub>N<sub>4</sub>) heterojunctions in Z-scheme for enhanced photocatalytic and electrochemical hydrogen evolution, *Appl. Catal. B Environ.* 228 (2018) 64–74.
- [17] K. Zhang, B. Jin, Y. Gao, S. Zhang, H. Shin, H. Zeng, J.H. Park, Aligned hetero-interface-induced 1T-MoS<sub>2</sub> monolayer with near-ideal gibbs free for stable hydrogen evolution reaction, *Small* (2019) 1804903.
- [18] H.I. Karunadasa, E. Montalvo, Y.J. Sun, M. Majda, J.R. Long, C.J. Chang, A molecular MoS<sub>2</sub> edge site mimic for catalytic hydrogen generation, *Science* 335 (2012) 698–702.
- [19] J. Liu, Y. Liu, D. Xu, Y. Zhu, W. Peng, Y. Li, F. Zhang, X. Fan, Hierarchical “nanoroll” like MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> hybrid with high electrocatalytic hydrogen evolution activity, *Appl. Catal. B* 241 (2019) 89–94.
- [20] Y. Li, K. Yin, L. Wang, X. Lu, Y. Zhang, Y. Liu, D. Yan, Y. Song, S. Luo, Engineering MoS<sub>2</sub> nanomesh with holes and lattice defects for highly active hydrogen evolution reaction, *Appl. Catal. B* 239 (2018) 537–544.
- [21] T.F. Jaramillo, K.P. Jorgensen, J. Bonde, J.H. Nielsen, S. Horch, I. Chorkendorff, Identification of active edge sites for electrochemical H<sub>2</sub> evolution from MoS<sub>2</sub> nanocatalysts, *Science* 317 (2007) 100–102.
- [22] Z.Z. Wu, B.Z. Fang, Z.P. Wang, C.L. Wang, Z.H. Liu, F.Y. Liu, W. Wang, A. Alfantazi, D.Z. Wang, D.P. Wilkinson, MoS<sub>2</sub> nanosheets: a designed structure with high active site density for the hydrogen evolution reaction, *ACS Catal.* 3 (2013) 2101–2107.
- [23] A. Bruix, H.G. Fuchtbauer, A.K. Tuxen, A.S. Walton, M. Andersen, S. Porsgaard, F. Besenbacher, B. Hammer, J.V. Lauritsen, In situ detection of active edge sites in single-layer MoS<sub>2</sub> catalysts, *ACS Nano* 9 (2015) 9322–9330.
- [24] M.V. Bollinger, J.V. Lauritsen, K.W. Jacobsen, J.K. Nørskov, S. Helveg, F. Besenbacher, One-dimensional metallic edge states in MoS<sub>2</sub>, *Phys. Rev. Lett.* 87 (2001) 196803.
- [25] Y. Yu, S.Y. Huang, Y. Li, S.N. Steinmann, W. Yang, L. Cao, Layer-dependent electrocatalysis of MoS<sub>2</sub> for hydrogen evolution, *Nano Lett.* 14 (2014) 553–558.
- [26] W.Y. Sun, P. Li, X. Liu, J.J. Shi, H.M. Sun, Z.L. Tao, F.J. Li, J. Chen, Size-controlled MoS<sub>2</sub> nanodots supported on reduced graphene oxide for hydrogen evolution reaction and sodium-ion batteries, *Nano Res.* 10 (2017) 2210–2222.
- [27] K. Chang, H. Pang, X. Hai, G. Zhao, H. Zhang, L. Shi, F. Ichihara, J. Ye, Ultra-small freestanding amorphous molybdenum sulfide colloidal nanodots for highly efficient photocatalytic hydrogen evolution reaction, *Appl. Catal. B-Environ.* 232 (2018) 446–453.
- [28] F. Li, J. Li, Z. Cao, X. Lin, X. Li, Y. Fang, X. An, Y. Fu, J. Jin, R. Li, MoS<sub>2</sub> quantum dot decorated RGO: a designed electrocatalyst with high active site density for the

- hydrogen evolution reaction, *J. Mater. Chem. A Mater. Energy Sustain.* 3 (2015) 21772–21778.
- [29] X. Ren, L. Pang, Y. Zhang, X. Ren, H. Fan, S. Liu, One-step hydrothermal synthesis of monolayer MoS<sub>2</sub> quantum dots for highly efficient electrocatalytic hydrogen evolution, *J. Mater. Chem. A Mater. Energy Sustain.* 3 (2015) 10693–10697.
- [30] D. Gopalakrishnan, D. Damien, M.M. Shaijumon, MoS<sub>2</sub> quantum dot-interspersed exfoliated MoS<sub>2</sub> nanosheets, *ACS Nano* 8 (2014) 5297–5303.
- [31] S.K. Park, D.Y. Chung, D. Ko, Y.E. Sung, Y. Piao, Three-dimensional carbon foam/N-doped graphene@MoS<sub>2</sub> hybrid nanostructures as effective electrocatalysts for the hydrogen evolution reaction, *J. Mater. Chem. A Mater. Energy Sustain.* 4 (2016) 12720–12725.
- [32] M. Chatti, T. Gengenbach, R. King, L. Spiccia, A.N. Simonov, Vertically aligned interlayer expanded MoS<sub>2</sub> nanosheets on a carbon support for hydrogen evolution electrocatalysis, *Chem. Mater.* 29 (2017) 3092–3099.
- [33] Y. Sun, F. Alimohammadi, D. Zhang, G. Guo, Enabling colloidal synthesis of edge-oriented MoS<sub>2</sub> with expanded interlayer spacing for enhanced HER catalysis, *Nano Lett.* 17 (2017) 1963–1969.
- [34] Y. Yan, B. Xia, N. Li, Z. Xu, A. Fisher, X. Wang, Vertically oriented MoS<sub>2</sub> and WS<sub>2</sub> nanosheets directly grown on carbon cloth as efficient and stable 3-dimensional hydrogen-evolving cathodes, *J. Mater. Chem. A Mater. Energy Sustain.* 3 (2015) 131–135.
- [35] D. Kong, H. Wang, J.J. Cha, M. Pasta, K.J. Koski, J. Yao, Y. Cui, Synthesis of MoS<sub>2</sub> and MoSe<sub>2</sub> films with vertically aligned layers, *Nano Lett.* 13 (2013) 1341–1347.
- [36] H. Wang, Z. Lu, S. Xu, D. Kong, J.J. Cha, G. Zheng, P.C. Hsu, K. Yan, D. Bradshaw, F.B. Prinz, Y. Cui, Electrochemical tuning of vertically aligned MoS<sub>2</sub> nanofilms and its application in improving hydrogen evolution reaction, *Proc. Natl. Acad. Sci.* 110 (2013) 19701–19706.
- [37] F. Gloaguen, J.M. Leger, C. Lamy, Electrocatalytic oxidation of methanol on platinum nanoparticles electrodeposited onto porous carbon substrates, *J. Appl. Electrochem.* 27 (1997) 1052–1060.
- [38] J. Ying, G.P. Jiang, Z.P. Cano, L. Han, X.Y. Yang, Z.W. Chen, Nitrogen-doped hollow porous carbon polyhedrons embedded with highly dispersed Pt nanoparticles as a highly efficient and stable hydrogen evolution electrocatalyst, *Nano Energy* 40 (2017) 88–94.
- [39] H.B. Zhang, P.F. An, W. Zhou, B.Y. Guan, P. Zhang, J.C. Dong, X.W. Lou, Dynamic traction of lattice-confined platinum atoms into mesoporous carbon matrix for hydrogen evolution reaction, *Sci. Adv.* 4 (2018).
- [40] L.B. Huang, L. Zhao, Y. Zhang, Y.Y. Chen, Q.H. Zhang, H. Luo, X. Zhang, T. Tang, L. Gu, J.S. Hu, Self-limited on-site conversion of MoO<sub>3</sub> nanodots into vertically aligned ultrasmall monolayer MoS<sub>2</sub> for efficient hydrogen evolution, *Adv. Energy Mater.* (2018) 1800734.
- [41] L. Liao, J. Zhu, X.J. Bian, L.N. Zhu, M.D. Scanlon, H.H. Girault, B.H. Liu, MoS<sub>2</sub> formed on mesoporous graphene as a highly active catalyst for hydrogen evolution, *Adv. Funct. Mater.* 23 (2013) 5326–5333.
- [42] Z. Hu, L. Wang, K. Zhang, J. Wang, F. Cheng, Z. Tao, J. Chen, MoS<sub>2</sub> nanoflowers with expanded interlayers as high-performance anodes for sodium-ion batteries, *Angew. Chem. Int. Ed.* 53 (2014) 12794–12798.
- [43] S.Y. Cho, S.J. Kim, Y. Lee, J.S. Kim, W.B. Jung, H.W. Yoo, J. Kim, H.T. Jung, Highly enhanced gas adsorption properties in vertically aligned MoS<sub>2</sub> Layers, *ACS Nano* 9 (2015) 9314–9321.
- [44] K. Ai, C. Ruan, M. Shen, L. Lu, MoS<sub>2</sub> nanosheets with widened interlayer spacing for high-efficiency removal of mercury in aquatic systems, *Adv. Funct. Mater.* 26 (2016) 5542–5549.
- [45] M. Sevilla, A.B. Fuertes, Direct synthesis of highly porous interconnected carbon nanosheets and their application as high-performance supercapacitors, *ACS Nano* 8 (2014) 5069–5078.
- [46] Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, MoS<sub>2</sub> nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction, *J. Am. Chem. Soc.* 133 (2011) 7296–7299.
- [47] J.X. Guo, F.F. Li, Y.F. Sun, X. Zhang, L. Tang, Oxygen-incorporated MoS<sub>2</sub> ultrathin nanosheets grown on graphene for efficient electrochemical hydrogen evolution, *J. Power Sources* 291 (2015) 195–200.
- [48] L. Ma, J. Ye, W. Chen, J. Wang, R. Liu, J.Y. Lee, Synthesis of few-layer MoS<sub>2</sub>-Graphene composites with superior electrochemical lithium-storage performance by an ionic-liquid-Mediated hydrothermal route, *ChemElectroChem* 2 (2015) 538–546.
- [49] B. Mohanty, M. Ghorbani-Asl, S. Kretschmer, A. Ghosh, P. Guha, S.K. Panda, B. Jena, A.V. Krasneninnikov, B.K. Jena, MoS<sub>2</sub> quantum dots as efficient catalyst materials for the oxygen evolution reaction, *ACS Catal.* 8 (2018) 1683–1689.
- [50] Y. Liu, Y. Zhu, X. Fan, S. Wang, Y. Li, F. Zhang, G. Zhang, W. Peng, (0D/3D) MoS<sub>2</sub> on porous graphene as catalysts for enhanced electrochemical hydrogen evolution, *Carbon* 121 (2017) 163–169.
- [51] A. Liu, L. Zhao, J. Zhang, L. Lin, H. Wu, Solvent-assisted oxygen incorporation of vertically aligned MoS<sub>2</sub> ultrathin nanosheets decorated on reduced graphene oxide for improved electrocatalytic hydrogen evolution, *ACS Appl. Mater. Interfaces* 8 (2016) 25210–25218.
- [52] J. Xie, J. Zhang, S. Li, F. Grote, X. Zhang, H. Zhang, R. Wang, Y. Lei, B. Pan, Y. Xie, Controllable disorder engineering in oxygen-incorporated MoS<sub>2</sub> ultrathin nanosheets for efficient hydrogen evolution, *J. Am. Chem. Soc.* 135 (2013) 17881–17888.
- [53] A. Petzold, A. Juhl, J. Scholz, B. Ufer, G. Goerigk, M. Fröba, M. Ballauff, S. Mascotto, Distribution of sulfur in Carbon/Sulfur nanocomposites analyzed by small-angle X-ray scattering, *Langmuir* 32 (2016) 2780–2786.
- [54] Y. Liu, X. Zhou, T. Ding, C. Wang, Q. Yang, 3D architecture constructed via the confined growth of MoS<sub>2</sub> nanosheets in nanoporous carbon derived from metal-organic frameworks for efficient hydrogen production, *Nanoscale* 7 (2015) 18004–18009.
- [55] D. Gopalakrishnan, D. Damien, B. Li, H. Gullappalli, V.K. Pillai, P.M. Ajayan, M.M. Shaijumon, Electrochemical synthesis of luminescent MoS<sub>2</sub> quantum dots, *Chem. Commun.* 51 (2015) 6293–6296.
- [56] S. Xu, D. Li, P. Wu, One-Pot, facile, and versatile synthesis of monolayer MoS<sub>2</sub>/WS<sub>2</sub> quantum dots as bioimaging probes and efficient electrocatalysts for hydrogen evolution reaction, *Adv. Funct. Mater.* 25 (2015) 1127–1136.
- [57] J. Benson, M. Li, S. Wang, P. Wang, P. Papakonstantinou, Electrocatalytic hydrogen evolution reaction on edges of a few layer molybdenum disulfide nanodots, *ACS Appl. Mater. Interfaces* 7 (2015) 14113–14122.
- [58] E.P. Nguyen, B.J. Carey, T. Daeneke, J.Z. Ou, K. Latham, S. Zhuiykov, K. Kalantar-zadeh, Investigation of two-solvent grinding-assisted liquid phase exfoliation of layered MoS<sub>2</sub>, *Chem. Mater.* 27 (2015) 53–59.
- [59] X. Li, X. Lv, N. Li, J. Wu, Y.-Z. Zheng, X. Tao, One-step hydrothermal synthesis of high-percentage 1T-phase MoS<sub>2</sub> quantum dots for remarkably enhanced visible-light-driven photocatalytic H<sub>2</sub> evolution, *Appl. Catal. B* 243 (2019) 76–85.
- [60] D. Escalera-López, Y. Niu, S.J. Park, M. Isaacs, K. Wilson, R.E. Palmer, N.V. Rees, Hydrogen evolution enhancement of ultra-low loading, size-selected molybdenum sulfide nanoclusters by sulfur enrichment, *Appl. Catal. B* 235 (2018) 84–91.
- [61] B. Yang, Y. Chen, Y. Cui, D. Liu, B. Xu, J. Hou, Over 100-nm-thick MoO<sub>x</sub> films with superior hole collection and transport properties for organic solar cells, *Adv. Energy Mater.* 8 (2018) 1800698.
- [62] K. Crowley, G. Ye, R. He, K. Abbasi, X.P. Gao, α-MoO<sub>3</sub> as a conductive 2D oxide: tunable n-type electrical transport via oxygen vacancy and fluorine doping, *ACS Appl. Nano Mater.* 1 (2018) 6407–6413.
- [63] H. Huang, J. Huang, W. Liu, Y. Fang, Y. Liu, Ultradispersed and single-layered MoS<sub>2</sub> nanoflakes strongly coupled with graphene: an optimized structure with high kinetics for the hydrogen evolution reaction, *ACS Appl. Mater. Interfaces* 9 (2017) 39380–39390.
- [64] Y.P. Li, Y.F. Yu, Y.F. Huang, R.A. Nielsen, W.A. Goddard, Y. Li, L.Y. Cao, Engineering the composition and crystallinity of molybdenum sulfide for high-performance electrocatalytic hydrogen evolution, *ACS Catal.* 5 (2015) 448–455.
- [65] J.D. Benck, Z.B. Chen, L.Y. Kuritzky, A.J. Forman, T.F. Jaramillo, Amorphous molybdenum sulfide catalysts for electrochemical hydrogen production: insights into the origin of their catalytic activity, *ACS Catal.* 2 (2012) 1916–1923.
- [66] A.P. Murthy, J. Theerthagiri, J. Madhavan, K. Murugan, Highly active MoS<sub>2</sub>/carbon electrocatalysts for the hydrogen evolution reaction-insight into the effect of the internal resistance and roughness factor on the Tafel slope, *Phys. Chem. Chem. Phys.* 19 (2017) 1988–1998.
- [67] D.Y. Chung, J.M. Yoo, S. Park, G.Y. Jung, J.S. Kang, C.-Y. Ahn, S.K. Kwak, Y.-E. Sung, Edge-terminated MoS<sub>2</sub> nanoassembled electrocatalyst via in situ hybridization with 3D carbon network, *Small* 14 (2018) 1802191.
- [68] Z. Chen, D. Cummins, B.N. Reinecke, E. Clark, M.K. Sunkara, T.F. Jaramillo, Core-shell MoO<sub>3</sub>-MoS<sub>2</sub> nanowires for hydrogen evolution: a functional design for electrocatalytic materials, *Nano Lett.* 11 (2011) 4168–4175.